

## CHEMICAL PROCESS

This invention relates to a process for making mixtures of ether carboxylic acids and more particularly to processes for making mixtures of 1-hydroxy-3-oxa-1,2,4,5-pentane tetracarboxylic acid and 3,6-dioxo-1,2,4,5,7,8-octane hexacarboxylic acids or salts thereof.

Polycarboxylic acids have long been known to be useful, usually in the salt form, as detergent builders or sequestrants. Also, ether carboxylates useful as metal sequestering and detergent builders have been known and are most desirable for their beneficial effects in laundering applications.

Because these ether carboxylates have such effective sequestering ability they have become attractive in recent times for the replacement of sodium tripolyphosphate which has long been the leading detergent builder or sequesterant. Examples of prior art efforts to provide ether carboxylates detergent builders or sequestrants are found in U.S. Pat. Nos. 3,635,830; 3,692,685 which relate to the use of oxydisuccinic acid salts as detergent builders. Another example of the prior art employing a carboxylate ether is found in U.S. Pat. No. 3,914,927 relating to carboxymethyloxysuccinates.

While these compounds in the prior art have utility as a builder or sequesterant in laundry detergent formulations it has been found that mixtures of certain low molecular weight ether carboxylates are more attractive and cost effective for such utility. In the field of detergent builders and sequestrants for laundry detergent formulations low cost of the components is extremely important because it is a very competitive market. While many ether carboxylate compounds have been found to be useful there is needed more economical manufacturing processes whereby such compounds can be economically produced in large volume.

There has been discovered a mixture of polycarboxylic acids or salts thereof, particularly the sodium salts, of 1-hydroxy-3-oxa-1,2,4,5-pentane tetracarboxylic acid (HOPTC) and 3,6-dioxo-1,2,4,5,7,8-octane hexacarboxylic acid (DOOHC) which are highly useful for detergent formulations as a sequesterant or builder. This mixture is prepared by reaction of a combination of maleate and D,L-tartrate salts catalyzed with calcium ion in strongly basic solution. Large amounts of calcium carbonate are produced as a by-product during purification of the product.

An important requirement of an economical process for producing ether carboxylate salts is the economical means to dispose of waste by-product calcium carbonate in an environmentally acceptable yet economical manner. To provide a more economical process it is desired that a use for such by-product calcium carbonate be found rather than discharging it as waste.

## SUMMARY OF THE INVENTION

In accordance with the process of this invention, a mixture of salts, mainly the calcium salt, of maleic acid and D,L-tartaric acid comprising from about 20 to 70% by weight in aqueous solution react together in the presence of salt forming cations of calcium and alkali metal cations.

The above-described aqueous reaction mixture is maintained at a temperature of from about 20° C. to about 120° C. for a time period sufficient to form a reaction product containing a mixture of HOPTC and DOOHC salts. The reaction mixture is treated to re-

move calcium ion for purposes of utility in detergent compositions such that the molar ratio of calcium to D,L-tartrate succinate products is less than 1:10. The removed calcium cation is recovered and recycled to catalyze additional reactions to produce such product.

In one aspect of this invention the recycle of calcium ion in the process of this invention eliminates the need to dispose of large quantities of solid waste. In another aspect of this invention the recycle of the calcium ion in the form of solid, unwashed filter cake reduces greatly the loss of product otherwise carried out of the production stream when solid waste disposal would be required. In yet another aspect of this invention, raw material requirements, particularly calcium, required to produce the HOPTC/DOOHC mixture are greatly reduced. It has been shown that repeated recycle of calcium ion does not cause any increase in calcium content of the desired HOPTC/DOOHC mixture even though it is critical for detergent use to maintain very low levels of calcium ion in the HOPTC/DOOHC mixture.

## DETAILED DESCRIPTION OF THE INVENTION

HOPTC/DOOHC compositions are disclosed in U.S. Pat. No. 4,663,071 to Busch et al and is incorporated herein by reference. It is noted in the patent referred to above that the calcium cations in aqueous reaction mixtures catalyze the reaction. It has been previously known to employ the catalytic calcium in the form of calcium hydroxide since an alkaline agent was also required. Calcium hydroxide would serve both purposes of providing the catalyst and hydroxyl ions to provide the required alkalinity.

In accordance with this invention the source of the catalytic calcium ions in the aqueous reaction mixture is provided by adding calcium salts of maleic and tartaric acids wherein the calcium is obtained from filter cakes formed from previous reaction mixtures. It has been found that the small amounts of by-products and residual HOPTC and DOOHC in the filter cakes do not upset the desired balance of the desired compounds in the final reaction product. Further, minor amounts of by-product malate, maleate fumarate and D,L-tartrate likewise are not deleterious to the use of recycled calcium salt forming cation. Fresh maleic and D,L-tartaric acids are added for makeup as needed to form a suitable reaction mixture.

## HOPTC/DOOHC FORMATION

The first step is the synthesis of HOPTC/DOOHC mixtures by the reaction in aqueous medium of maleate and D,L-tartrate reactants comprising both monovalent cation and calcium salts of maleic acid and D,L-tartaric acid. As noted above, the total amount of maleate plus D,L-tartrate reactants in the aqueous reaction mixture will generally range from about 20% to about 70% by weight of the mixture, more preferably from about 50% to about 65% by weight. In accordance with this invention, calcium maleate is provided by first reacting maleic acid with calcium carbonate provided by earlier reactions as will be more fully described below. The D,L-tartrate is provided by hydroxylation of maleic anhydride in the presence of a catalyst and hydrogen peroxide by known means. One portion of the D,L-tartaric acid employed in the synthesis reaction is taken from the neutralized hydroxylation reaction product